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Mechanisms and Reaction Pathways in MEA Degradation; A Computational Study

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Abstract

The mechanistic details on formation of HEGly and HEPO in MEA degradation are studied using the ab initio and density functional theory methods. The energetics of various pathways leading to formation of HEGly and HEPO are investigated. The addition of glyoxalic acid to MEA and simultaneous proton transfer results in a carbinolamine intermediate. This intermediate undergoes dehydration to generate zwitterion or imine. The hydrogenation of the resulting imine or zwitterion to form HEGly is found to be the rate determining step of the reaction.

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1. Introduction

Reaction pathways and reaction mechanisms are of crucial importance to understand the degradation phenomenon observed in chemical absorption of CO₂ in amine solvents. In this work, theoretical investigations are performed to examine the structures of transition states to analyse which reactants and products are connected by a transition structure, and to calculate the reaction energies in the oxidative degradation of MEA. Many primary and secondary degradation compounds and mechanisms for their formation have been suggested in literature.¹⁻³ Recently da Silva et al⁴ in their pilot plant study on absorption of CO₂ in MEA has reported the formation of N-(2-hydroxyethyl)-glycine (HEGly) and 4-(2-hydroxyethyl)-2-piperazinone (HEPO) as degradation compounds in relatively high amounts. This work mainly focuses on understanding the mechanisms involved in the formation of these two degradation compounds. Vevelstad³ and Gouedard et. al.⁵ have suggested mechanisms for these degradation

compounds in the MEA-CO₂-H₂O system. In this work, computational chemistry methods are employed to study these mechanisms and possible reaction pathways leading to degradation products. Fig. 1 shows a graphical representation of the reaction coordinate plotted against the free energy, which illustrates how the activation energy for a single step in a reaction is calculated.⁶

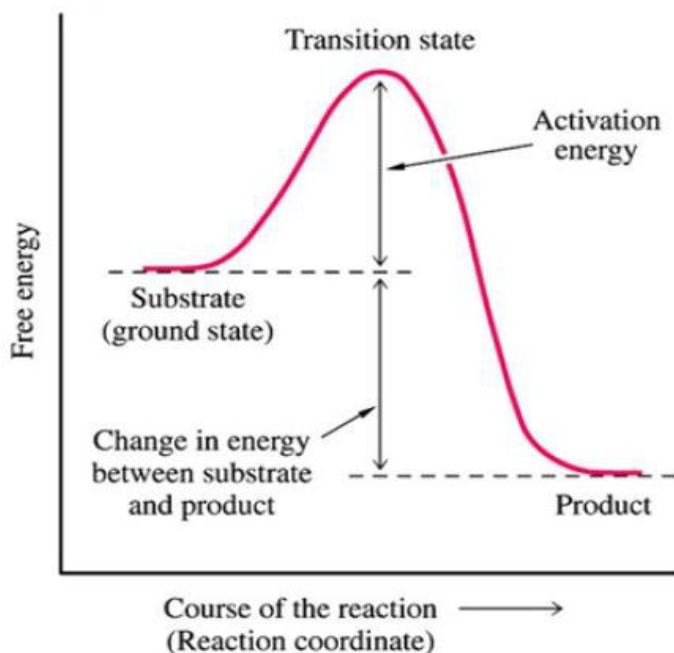


Figure 1: Schematic plot of reaction free energy as a function of reaction coordinate [taken from Davis and Carpenter, 1997]⁷.

2. Computational Details

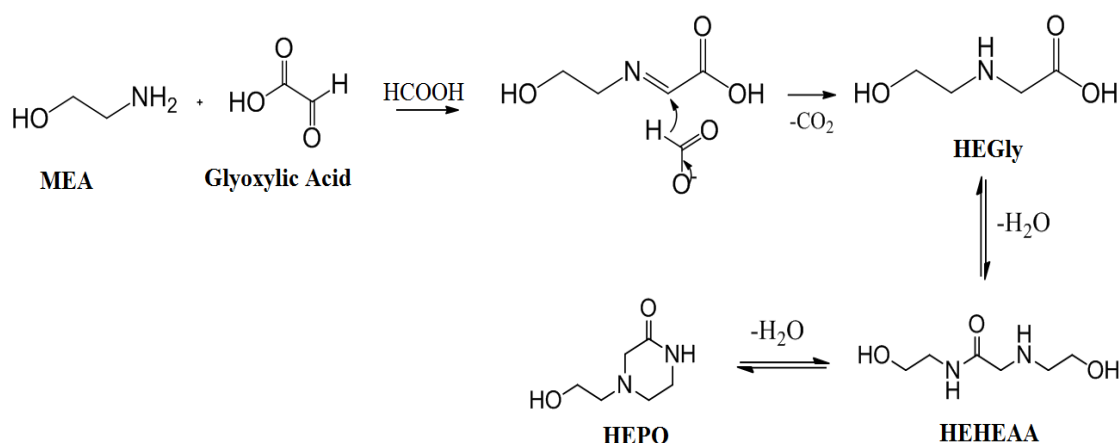
All the transition state structures and reactants were fully optimized, in the gas phase at B3LYP/6-31+G(d,p) level of theory using the Gaussian09⁸ and Gaussview suite⁹ of quantum chemical programs. Further, the gas-phase geometries were re-optimized at the PCM(water)/B3LYP/6-31+G(d,p) level of theory using Tomasi's polarized continuum model (PCM).^{10,11} The solvation energies are considered to be more sensitive w.r.t electron density and shape of the molecule. A suitable theoretical model coupled with good basis sets should be chosen to have estimates of solvation within acceptable accuracy.¹²

By evaluating the vibrational frequencies, optimized geometries obtained were characterized as stationary points on the potential energy surface (PES) at B3LYP/6-31+G(d,p) level of theory. The transition states were characterized by one and only one imaginary frequency which are confirmed to represent accurate reaction coordinate. 10% displacement on the transition state geometry along the direction of the imaginary vibrational frequency is carried out. The shifted geometry is submitted for re-optimization using 'calcfc' option available in Gaussian 09. This procedure confirms that we have obtained accurate transition state geometry and that it connects reactants and products on both sides of the transition state. The intrinsic reaction coordinate (IRC) calculations were done at the B3LYP/6-311+G** level of theory to further confirm the transition states.^{13,14} The intrinsic reaction coordinates (IRCs) were also calculated to generate the path of the reaction: reactants to transition states to products.

3. Results and Discussion

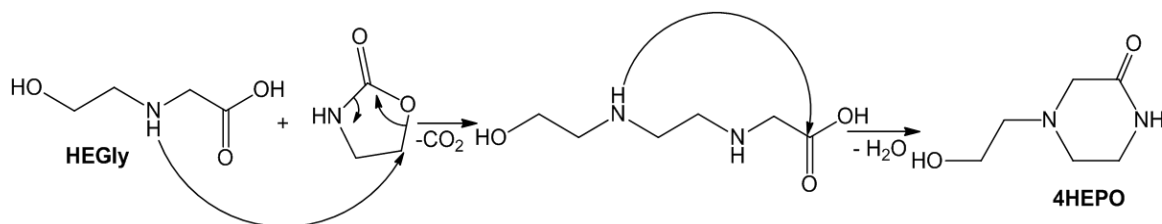
MEA undergoes two types of degradation in post combustion CO₂ capture process: Oxidative degradation and thermal degradation. Mechanisms for some of the degradation products found while using MEA as a solvent are given in literature, but still there are some uncertainties for few mechanisms suggested. According to experimental studies by da Silva et al.⁴, it has been found that HEPO and HEGly are major degradation compounds for MEA and understanding the mechanisms behind the formation of these degradation compounds is therefore of great interest. Knowing the reaction mechanisms behind the formation of these degradation compounds would help in understanding the reaction chemistry of the solvent and measures can be taken to prevent this degradation of solvent.

There are one mechanisms suggested in the literature for the formation of HEGly and two mechanisms are suggested for the formation of HEPO.



Scheme 1: Proposed Mechanism of MEA Degradation to HEGly and HEPO proposed by Vevelstad².

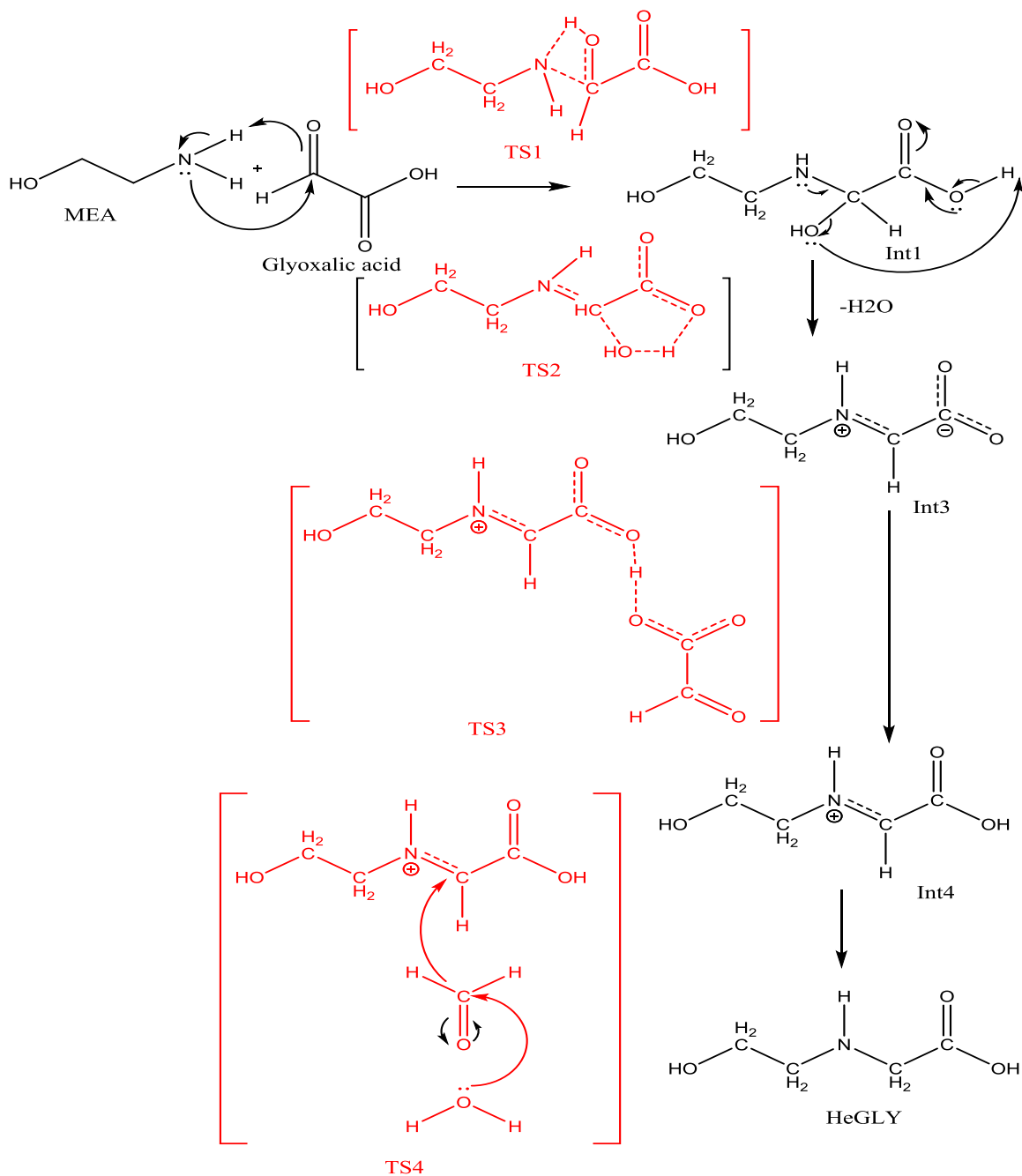
Vevelstad³ suggested the mechanism of formation of HEGly and HEPO as shown in scheme 1. Gouedard et al.⁵ have suggested the mechanism for formation of HEPO as given in Scheme 2.



Scheme 2: Proposed Mechanism of formation of HEPO from HEGly by Gouedard, C et. al.⁹

In the present work, different pathways for the formation of HEGly are investigated by using theoretical quantum mechanical calculations. In Scheme 3, schematic details of reaction mechanism, including transition states, for the formation of HEGly is presented. Transition state 1 (TS1) involves addition of glyoxalic acid to MEA with

simultaneous proton transfer to form carbinolamine intermediate. This intermediate undergoes dehydration to generate zwitterion or imine, which is second transition state for the reaction. In the second transition state if the



Scheme 3: Transition states involved in the formation of HeGLY from HEGly and Glyoxalic acid.

water is removed by combining terminal carboxyl hydrogen with hydroxyl group from the carbon atom in N-C bond, it give rise to a zwitterion formation as shown in scheme 3 above. On the other hand, if hydroxyl group and hydrogen are removed from adjacent N-C bond, it give rise to an imine, which is not shown in scheme 3 but transition state obtained for the same is given in Fig. 2 below. Transition state 3 is acid base hydrogen shift, which being an instantaneous step, does not give a stable transition state. The transition state accompanying the hydrogenation of resulting imine or zwitterion to form HEGly is found to be the rate determining step of the reaction.

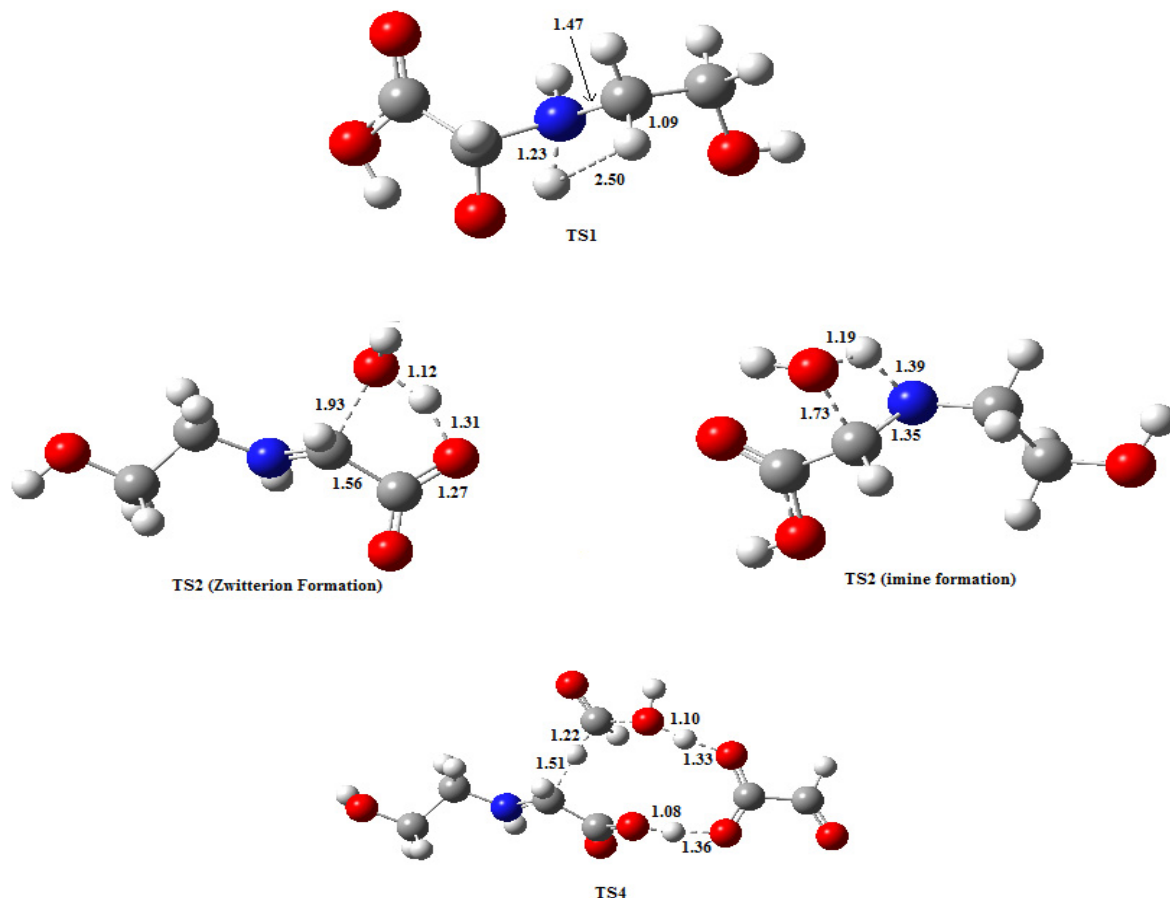


Fig. 2: The B3LYP/6-31+G(d,p) optimized transition state geometries for step I, II and IV.

In Fig. 2, TS1 involves the addition of glyoxalic acid to MEA and simultaneous proton transfer, which results in a carbinolamine intermediate. TS2 involves dehydration step to generate zwitterion. TS4 involves hydrogenation of resulting zwitterion to form HEGly with the active stabilization by water and glyoxalate ion. Optimized bond lengths at the B3LYP/6-31+G(d,p) level of theory are given for the bonds involved in transition state. Distances are in Å.

In Table 1, computed activation free energies i.e free energy with respect to separated reactants are given for different transition states obtained in present work. Transition state 1, as shown in Fig. 2, involving MEA and glyoxalic acid addition and hydrogen transfer has an activation free energy barrier of 32.4 Kcal/mol in the gas phase and 24.8 in aqueous phase. TS1 involves formation of four membered ring for the proton transfer, which is a strained geometry as four membered ring is not very stable. TS1 should be minimised in energy by the active

assistance of co-catalyst molecule to make bigger strain-less rings at the transition state structure. Transition state 2, involving water removal for the generation of zwitterion has an activation free energy barrier of 19.7 Kcal/mol in gas phase. This means that this step can occur easily at room temperature. In the absorber and stripper in PCC units, we have temperature range of 60-120 °C, at which temperature this step is expected to be very fast. TS3 involves acid-base proton shift, which is an instantaneous step and therefore the transition state for this step is not stable.

Table 1: Computed Activation Barriers^a for TS1, TS2 and TS4 obtained at B3LYP/6-31+G(d,p) Level of Theory for the Formation of HEGly.

Transition State	Activation Free Energy (Kcal/mol)	
	Gas Phase (B3LYP/6-31+G(d,p)	Aq. Phase (PCM(water)/B3LYP/6-31+G(d,p)
TS1	32.4	24.8
TS2 (Zwitterion)	19.7	17.1
TS2 (imine)	55.23	49.8
TS4_formaldehyde	37.32	36.56
TS4_Glyoxalic acid	40.27	38.8
TS4_Formic acid	51.44	42.4

^a Barriers with respect to the separated reactants. ^b All energies refer to the optimized geometries at B3LYP/6-31+G(d,p) Level of Theory.

Transition state 4 involves hydrogenation of intermediate obtained after step 3 to form HEGly. In Fig.2, TS4 is shown where formaldehyde is giving its hydride to the –CH group of the intermediate obtained in Step 3, in the presence of water and glyoxalate ion. Water and glyoxalate ion are stabilising the transition state by formation of hydrogen bonds. The energy of this TS is given in table 4 as energy for “TS4_formaldehyde”, as formaldehyde is involved in donating hydride in this transition state. We obtained lowest energy barrier in this step as compared to other two in which glyoxalic acid and formic acid are giving their hydride for hydrogenation. This step is rate determining step of the reaction. Thus involvement of stabilizing species can lower the energy barrier of transition state.

4. Conclusion

The exploration of various viable pathways leading to the HEGly formation by the reaction of MEA with glyoxalic acid has been carried out. From the calculated activation barriers i.e barriers w.r.t to separated reactants shows that the hydrogenation of imine or zwitterion intermediate, formed in third step, is the rate-limiting step in this reaction. A number of transition state searches in transition state 4 involving hydride transfer from different ancillary molecules i.e formaldehyde, glyoxalic acid and formic acid have been performed. It has been seen that transition state involving formaldehyde as a hydride donor for hydrogenation step to form HEGly is most favoured energetically. The energy barriers in hydrogenation step leading to formation of HEGly, depends mainly on the nature of hydride donor molecule and extent of its hydrogen bonding with actively added co-catalyst. From this work, we can also conclude that theoretical investigations of mechanisms of degradation products would improve the understanding of CO₂ absorption systems and also would be helpful to validate the proposed mechanisms in the literature

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